Studies of cyclic and linear poly(dimethylsiloxanes): 27. Bulk viscosities above the critical molar mass for entanglement

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Low-shear bulk viscosity measurements are presented for sharp (narrow distribution) cyclic and linear poly(dimethylsiloxane) (PDMS) fractions in the number-average molar mass range 5×10^2 to 3.2×10^4 g mol^{-1}. The results allow the first estimate to be made of the critical molar mass for entanglement, M_c, for PDMS rings. This value does not differ significantly from that of the linear polymer. The viscosity–molar mass relationships are reported here for ring and chain samples above and below M_c.

(Keywords: PDMS; viscosity; molar mass)

INTRODUCTION

The preparation and physical investigation of sharp (narrow distribution) fractions of cyclic poly(dimethylsiloxane) (PDMS) have been reported in detail in previous papers in this series[1]. Cyclic macromolecules have been prepared with number-average degrees of polymerization up to 10×10^2 and their ring structures have been established by dilute-solution viscosity, bulk viscosity, low-angle neutron scattering, quasielastic light scattering, network trapping and diffusion investigations.

The viscometric behaviour of bulk polymers can be divided into two distinct regions, that below and that above the critical molar mass for entanglement, M_c. This molar mass represents the point at which the sample begins to show the presence of a temporary entanglement network structure. Above M_c, the mobility of a molecule (and hence the viscosity) is no longer determined by an average friction coefficient, since now the coupling loci also restrict mobility. This is the regime treated by the reptation models[2–4].

EXPERIMENTAL

Cyclic and linear PDMS fractions were prepared and characterized by methods described previously[5,6] (see Table 1). A Contraves Low Shear 30 Rotational Rheometer was used for the measurements. This is a highly sensitive torque-measuring system that can generate 30 fixed shear rates $\dot{\gamma}$, and using Couette geometry these lie in geometric progression through the range 10^2 to 10^{-2} s^{-1}. The viscosities for the individual ring and chain fractions were determined in the number-average molar mass range $5 \times 10^2 < M_n < 3.2 \times 10^4$ g mol^{-1} at a range of shear rates.

RESULTS

As would be expected, the measured viscosities were found to be effectively independent of $\dot{\gamma}$, since silicone oils are used as Newtonian viscosity standards. For this reason, viscosities are henceforward reported at the single

Table 1 Characterization details of ring and chain samples (shear rate $= 8.11$ s^{-1})

Rings			Chains		
n_n	M_w/M_n	η at 298 K (cP)^a	n_n	M_w/M_n	η at 298 K (cP)
14.0	1.02	9.51	14.5	1.03	3.94
22.2	1.02	18.25	22.6	1.01	6.64
			30.0	1.02	9.44
32.0	1.06	17.92	32.0	1.04	9.67
40.1	1.01	20.26	40.3	1.01	12.01
57.0	1.03	25.72	57	1.04	15.68
			72	1.06	21.07
86	1.02	27.02	86	1.08	26.77
99	1.05	30.47	102	1.02	31.76
114	1.01	34.09	112	1.06	32.48
138	1.04	40.76			
188	1.06	49.45	163	1.05	52.18
206	1.04	58.53	203	1.05	67.30
			250	1.03	82.81
334	1.01	65.85	330	1.05	138.69
513	1.04	121.81			
582	1.08	194.97	591	1.04	335.30
719	1.06	359.60	682	1.05	678.24
866	1.08	783.76	818	1.12	968.59

^{a} 1 cP $= 10^{-3}$ kg m^{-1} s^{-1}

Table 2 Compensatory temperatures calculated for constant $T - T_g$

n_n	T_g (K) from d.s.c.	Compensation temperature (K)
Chains		
14.5	140.1	288.4
22.6	143.4	291.7
30.0	143.6	291.9
40.3	146.1	294.4
57.0	147.6	295.9
72.0	148.1	296.4
86.0	148.6	296.9
102	149.1	297.4
112	149.0	297.3
203	149.5	297.8
250	149.5	297.8
330	149.4	297.7
393	149.7	298.0
682	149.7	298.0
591	149.7	298.0
818	149.7	298.0
Rings		
14.0	156.8	305.1
22.2	155.0	303.3
32.0	152.7	301.1
40.1	152.0	300.3
57.0	151.3	299.6
86	150.8	299.1
99	150.5	298.8
114	150.5	298.8
188	150.4	298.7
206	150.3	298.6
334	150.2	298.5
513	150.2	298.5
582	150.2	298.5
719	150.3	298.6
866	150.3	298.6

shear rate of 8.1 s^{-1}. In practice, this corresponds to zero-shear-rate viscosity $\eta_{r,0}$ for rings and $\eta_{l,0}$ for linear chains. At 298 K the log η vs. log n_n plot (where n_n is the number average of skeletal bonds) shows a crossover point at approximately 100 skeletal bonds. Below this crossover point, the viscosity ratio of ring $\eta_{r,0}$ to equivalent chain $\eta_{l,0}$ is ~ 2.5, whereas at higher molecular weights a ratio 0.47 is found at ~ 330 skeletal bonds.

It had been suggested that the crossover in the plot was due entirely to the fact that the viscosity values had not been reduced to the same segmental mobility, i.e. that the effect of the chain ends had not been taken into account. One way to compensate for the change in molecular mobility was to evaluate the viscosities at constant $T - T_g$. This was possible since glass transition temperatures (T_g) for both ring and chain fractions were known from differential scanning calorimetry studies. The viscosities of the samples were therefore redetermined at the temperatures shown in *Table 2*, to make $T - T_g$ constant (148.3 K). However, correcting for constant segmental motion had very little effect on the viscosity values, and the general shape of the log η versus log n_n plot remained the same, but the viscosity function is somewhat more linear in the low-molar-mass region for chains, as would be expected (see *Figure 1*).

At higher molar masses the log η vs. log n_n plot then undergoes a sudden change in slope for both ring and chain fractions. This change shows that the critical molar mass for entanglement has been reached. Below M_c the slope for the log η vs. log n_n plot for the linear fractions approaches 1.05 (± 0.05). The ring samples in the same

molar mass region follow a near-linear plot with a slope 0.6 (± 0.05). In the molar mass region greater than M_c, the viscosities of the linear siloxanes increase with the power 3.21 (± 0.05). The cyclic molecules show similar behaviour above M_c and give only slightly lower values than those of their linear analogues. The cyclic fractions follow a 3.46 (± 0.05) power-law relationship with molar mass. By extrapolating the two branches in the plots and calculating the point of intersection, values of M_c for ring and chain PDMS molecules were determined to be $\sim 1.70 \times 10^4$ and $\sim 1.66 \times 10^4$ respectively (see *Figure 1*).

DISCUSSION

The bulk viscosity values obtained compare well with other previously quoted values[7-11]. The explanation as to why the viscosities of the rings are higher than those of the corresponding chains in the low-molar-mass region is believed to result from configurational restrictions in the ring molecules. This makes them appear less flexible and leads to a reduction in segmental mobility, which therefore results in a higher viscosity.

In an early paper, Bueche[12] had predicted that in the region below M_c the ratio of the bulk viscosity of a branched polymer to that of a linear polymer would be equivalent to the ratio of their respective mean-square radii of gyration. If this theoretical approach is applied to ring molecules, the ratio of η_r to η_l should be equivalent to $\langle s^2 \rangle_r / \langle s^2 \rangle_l = 0.50$ (which has been well verified experimentally[1]). The experimentally determined viscosity values show that in the region of 330 skeletal bonds the value of this ratio is indeed being approached.

It has also been predicted for linear species that below M_c the viscosity should be directly proportional to the molar mass of the sample[13-15]. Experimental values are in excellent agreement with this prediction. Above the theoretical M_c it is found experimentally[14] that the viscosity should be proportional to a 3.4–3.5 molar mass power law. The Doi–Edwards[2] theory of reptation gives $\eta \propto M^3$ for very high M; Doi has discussed the discrepancy and shown $\eta \propto M^{3.4}$ for lower M. The linear
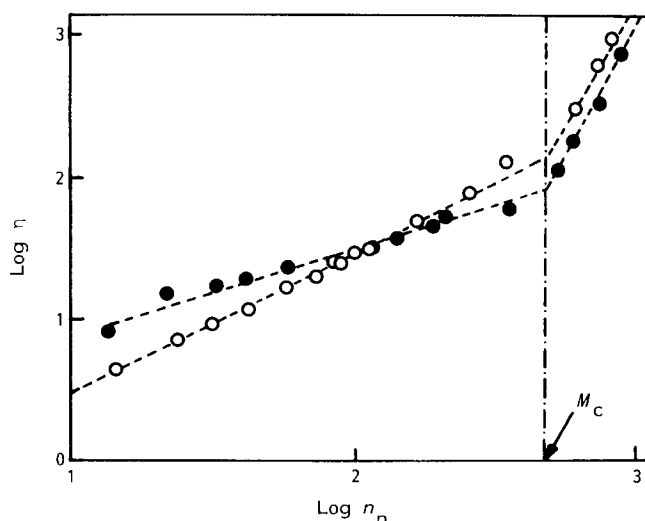

Figure 1 Plot of log η against log n_n for ring ($\bullet$) and chain ($\bigcirc$) PDMS fractions at $T - T_g$ (as shown in *Table 2*)

fractions above M_c give a value of 3.21 (± 0.05), which compares well with power relationships given by other polymeric systems. The slightly lower value for the linear polymers reflects the small number of fractions investigated. No theoretical predictions have been proposed for viscosity–molar mass relationships for ring molecules. Above M_c, η_r is proportional to $M^{3.46}$, and this relationship shows remarkable similarity to the theoretical prediction for linear systems, although again it is noted that the number of cyclic samples available for investigation in this region is restricted.

The critical entanglement molar mass for linear siloxanes has been determined to be $\sim 1.66 \times 10^4$. This is also slightly lower than previously reported values[14,16-18], i.e. 2.1×10^4. This, like the slightly lower slope, can be explained by the fact that the molar masses studied above M_c were really in the transition region for the change-over from a slope of 1.0 to a slope of 3.4. It is interesting to note, though, that the value quoted here for M_c corresponds to approximately twice the value quoted by Graessley[14] for M_e ($\sim 8.1 \times 10^3$), where M_e is the molar mass between entanglements in a melt, calculated from the plateau modulus. Many polymeric systems are known to show the relationship $M_c = K M_e$ (where $1.7 < K < 2.5$).

Perhaps the most interesting feature of *Figure 1* is the appearance of a critical molar mass for cyclic PDMS. This is the first set of data that have enabled a value of M_c for such flexible cyclic molecules to be determined. The M_c values for cyclic PDMS appears not to differ significantly from that of the linear polymers. This finding is in agreement with the results presented by McKenna *et al.*[19] for cyclic and linear polystyrene. Their results also exhibit slightly lower cyclic melt viscosities than for the corresponding linear polystyrenes above M_c.

The results presented here are expected to have important implications for aspects of reptation theory, where the motion of a macromolecule above M_c is likened to the movement of a snake. Motion is confined to a 'tube', which is defined by the entanglements of neighbouring molecules, and only the ends of the chain have a choice of direction in which they move. Using such an approach, it follows that ring polymers cannot reptate since they have no free ends. On this basis, ring fractions above M_c would be predicted to have substantially greater viscosities than their linear counterparts and might well represent an infinitely viscous system. The data presented here show that the situation is quite different. Chain-end effects are shown to be far less important than was suggested, and motion appears to be independent of chain-end movement. This would appear to be a reasonable assumption since a long enough chain could form loops that could act as 'equivalent chain ends'. These loops would be present in both ring and chain systems and therefore may account for the similar viscometric behaviour of cyclic and linear fractions above M_c. A new model for motion of flexible ring and chain polymers in the melt appears to be required. In this connection, Doi[4] has suggested a tube renewal concept in order to interpret the melt characteristics of star branched polymers. Thus the tube itself would represent the presence of all other rings, whilst the one in the tube moves by the rearrangement of this tube, rather than by reptation down the tube.

APPRECIATION

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